

Pervaporation of Water/Alcohol Mixtures Through Chitosan/Cellulose Acetate Composite Hollow-Fiber Membranes

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ABSTRACT: For the purpose of separating aqueous alcohol by the use of pervaporation technique, a composite membrane of chitosan (CT) dip-coated cellulose acetate (CA) hollow-fiber membranes, CT-*d*-CA, was investigated. The effects of air-gap distance in the spinning of CA hollow-fiber membranes, chitosan concentration, and sorts of aqueous alcohol solutions on the pervaporation performances were studied. Compared with unmodified CA hollow-fiber membrane, the CT-*d*-CA composite hollow-fiber membrane effectively increases the permselectivity of water. The thickness of coating layer increases with an increase in chitosan concentration. As the concentration of chitosan solution in-

creased, the permeation rate decreased and the concentration of water in the permeate increased. In addition, the effects of feed composition and feed solution temperature on the pervaporation performances were also investigated. The permeation rate and water content in permeate at 25°C for a 90 wt % aqueous isopropanol solution through the CT-*d*-CA composite hollow-fiber membrane with a 5-cm air-gap distance spun, 2 wt % chitosan dip-coated system were 169.5 g/m² h and 98.9 wt %, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1562–1568, 2004

Key words: chitosan; coating; membranes

INTRODUCTION

Membrane techniques with easy operation and high energy savings have been one skills used in separating mixtures. The pervaporation separation technique through membrane is recognized as an efficient separation method especially for liquid mixtures with an azeotrope, close boiling point, isomers, or heat-sensitive.^{1–2} The separation of aqueous alcohol mixture by a pervaporation technique using a dense homogeneous polymer membrane was recently given much attention.^{3–4} One of the disadvantages of a dense homogeneous membrane for the pervaporation separation is the low permeation rate, especially with highly selective membrane materials. For industrial use, membranes of pervaporation with high flux and high selectivity are desired. Therefore, several methods of membrane preparation may be used to improve the separation performances such as surface modification, blending, copolymerization, and grafting a selective species onto an inert film.^{5–9}

Composite membranes, which are composed of two or three layers—a dense selective skin layer and a microporous support layer with/without nonwoven fabrics substrate, were recently widely used to improve the separation performances.^{10–13} Some of pervaporation plants were constructed over the last decade by using GFT membranes. The GFT established the commercial base pervaporator in Germany by the use of crosslinked poly(vinyl alcohol) (PVA) composite membrane. The advantage of the composite membranes is that each layer can be optimized independently to obtain optimal membrane separation performances with respect to flux, selectivity, and stability. In composite membranes, the top layer and support layer originated from different polymeric materials. Several methods were developed to achieve this, such as dip-coating, interfacial polymerization, and plasma polymerization.¹⁴

Wang et al.¹¹ investigated the dehydration of organic solvents by pervaporation by using alginate dip-coated polyacrylonitrile (PAN) microporous membranes. They showed that amination of the sublayer improved pervaporation performances of the composite membrane greatly. Karakane et al.¹⁵ studied the separation of a polyelectrolyte complex consisting of poly(acrylic acid) and a polycation. They reported that high flux and selectivity could be obtained for a feed

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concentration of 95 wt % ethanol aqueous solution. For improving the ethanol selectivity in pervaporation, Matsuda et al.¹⁶ used silicone rubber dip-coated on silicalite membrane.

The supporting layer of composite membrane should be provided with high flux to avoid the decrease permeation rate of composite membranes. In general, asymmetric flat membrane as well as hollow-fiber membrane can be used as substrate. Hollow-fiber membranes possess many more advantageous characteristics than the flat ones.² Nevertheless, little research literature has been found on the systematic study on pervaporation of aqueous organic mixtures through hollow-fiber membranes^{17–20} despite their wide acceptance in other separation processes such as gas separation and ultrafiltration processes.^{21–26} We also investigated the effect of additives (surfactant or cosolvent) in the spinning solution on the morphology and separation performances of polysulfone (PSf) hollow-fiber membranes through vapor permeation or pervaporation operation.^{27–28} It showed that the morphology and separation performances of PSf hollow-fiber membranes could be affected by adding additives in spinning solution.

In this study, chitosan (CT) dip-coated cellulose acetate (CA) hollow-fiber membranes (CT-*d*-CA) composite were fabricated to investigate the separation performances of water/alcohol mixtures through pervaporation. It is recognized that CA is a good membrane material for reverse osmosis, ultrafiltration, and microfiltration, and chitosan is the *N*-deacetylated product of chitin, a natural polymer that can be extracted from outer shells of crustaceans. Chitosan is a linear polymer composed primarily of glucosamine. In this investigation, chitosan was chosen as the polymer material of the dip-coated layer because of its favorable permselectivity to water and solvent stability as well as good film-forming property.^{29–31} The purpose of this article was to attempt to prepare CT-*d*-CA composite hollow-fiber membranes by dip-coated chitosan solution on the outer surface of porous CA hollow-fiber membrane to explore the pervaporation separation performances of aqueous alcohol mixtures. Moreover, the effect of feed composition and feed solution temperature on pervaporation performances was also investigated.

EXPERIMENTAL

Materials

Cellulose acetate (molecular weight, 50000 with acetyl content 39.8 mol %), used as the composite hollow-fiber supporting matrix in this study, was purchased from Aldrich Co. (USA). The dip-coated polymer solution, chitosan, with 85% *N*-deacetylation degree was supplied by Sigma Co. (Ateenheim, Germany). The

solvent, *N,N*-dimethylformamide (DMF Tedia Co., Fairfield, OH), and acetic acid (Fluka Co., Buchs, Switzerland) were of reagent grade and used without further purification. Glutaraldehyde (Fluka Co.) was used as crosslinking agent in this study.

Spinning of CA hollow fiber

CA polymer and solvent (DMF) were mixed in a flask under agitation to form a 25 wt % homogenous CA polymer solution, which was then stored at least 1 day. The homogenous polymer solution was then poured into the dope tank of spinning frame and kept overnight.

CA hollow-fiber membranes were fabricated by a dry/wet spinning process. The spinning dope was extruded under 1 atm pressure through a spinneret. The dimensions of this spinneret were 0.6 and 0.4 mm for outer diameter (OD) and inner diameter (ID), respectively. The bore liquid was introduced by a metering pump. The degassed homogenous polymer solution and bore liquid were extruded through the spinneret die to form a nascent hollow-fiber membrane and then passed through an air gap from 5 to 75 cm before entering into the coagulation bath of water. There were no external elongation stresses except gravity was applied to the nascent hollow-fiber membranes. The hollow fiber was washed thoroughly with water to remove the residual solvent for 2 h and then was kept in 50 wt % aqueous glycerin solution to prevent the collapse of the porous structure for 3 days. Table I reveals the detailed process parameters and spinning conditions.

Fabrication of CT-*d*-CA composite hollow-fiber membrane

CT-*d*-CA composite hollow-fiber membranes were formed by dip-coating the chitosan solution on the outer surface of CA hollow fiber. Chitosan solution was prepared by dissolving chitosan flakes into 2 wt % aqueous acetic acid solution to form 1.5–2.5 wt % chitosan solution. The solution was filtered to remove any undissolvable solids or impurities and allowed to stand for about half a day to remove the air bubbles. Then, they were dip-coated onto CA hollow-fiber membrane outer surface and dried at 80°C for 40 min. After drying, CT-*d*-CA composite hollow-fiber membranes were dipped into 0.12 wt % aqueous glutaraldehyde solution at 30°C. Then, the CT-*d*-CA composite hollow-fiber membranes were cured at 80°C.

SEM observation of hollow-fiber membrane

The outer surface morphologies of CA hollow-fiber membranes and cross-section morphologies of CT-*d*-CA composite hollow-fiber membranes were ob-

TABLE I
Process Parameters and Spinning Conditions

Process parameters/Spinning conditions	Value
Spinning solution	CA/DMF
Polymer concentration (by weight)	25 wt %
Spinning temperature (°C)	Ambient temperature
Spinneret OD/ID	0.6/0.4 mm
Spinning solution pressure	1 atm
Bore liquid	H ₂ O
Air gap distance	5–75 cm
External coagulant	H ₂ O
External coagulation bath temperature (°C)	Ambient temperature
Posttreatment process	Washed thoroughly with water for 2 h Keep in 50 wt % aqueous glycerin solution for 3 days

served with a scanning electron microscopy (SEM, Hitachi model S4700). The fiber samples were immersed in liquid nitrogen to fracture and then were sputtered with platinum.

Module fabrication and pervaporation tests

The hollow-fiber module for pervaporation test consisted of five fibers. The fiber bundles were plotted in a 5-min rapid solidified epoxy resin binder. The effective length of every hollow fiber for pervaporation was 8 cm.

The procedure and the apparatus used in the pervaporation experiments were the same as described in previous work.²⁸ The feed solution was pumped into the shell side of the module and the permeates came out from the lumen of the fibers. The permeation rate was determined by

$$P = W/(A \times t) \quad (1)$$

where P , W , A , and t represent the permeation rate ($\text{g}/\text{m}^2 \text{ h}$), weight of permeate (g), the effective hollow-fiber area base on the outside diameter of fiber (m^2), and operation time (h), respectively. A vacuum pump maintained the downstream pressure at 3–5 mmHg. The permeation rate was determined by measuring the weights of permeate. The compositions of the feed solutions and permeates were measured by gas chromatography (GC China Chromatography 8700).

RESULTS AND DISCUSSION

Effect of air gap on the pervaporation performances of CA hollow-fiber membrane

Separating aqueous alcohol mixtures by using pervaporation technique, a composite membrane of CT-*d*-CA, was prepared. There is considerable evidence to show that the separation performance of the supporting layer of composite membrane plays a part in the transport process of pervaporation. Thus, the effect of

air gap on the pervaporation performances of CA hollow-fiber membrane will be discussed first. In general, the solvent evaporation rate and solvent/nonsolvent exchange rate dominates the membrane morphology during the dry- and wet-phase-inversion procedures, respectively. In the hollow-fiber membrane formation process, the air-gap distance was similar to the dry period in the dry-wet-phase inversion.

The effect of air-gap distance on the pervaporation performances of a 90 wt % aqueous ethanol solution at 25°C through the CA hollow-fiber membrane is shown in Figure 1. It shows that the permeation rate decreases and the water content in permeate increases with an increase in the air-gap distance. These results can be explained from the viewpoint of membrane morphology. It is widely accepted that the separation performance of membranes is strongly related to the membrane structure. To investigate the effect of air-gap distance on the hollow-fiber membrane structure, SEM studies were made. Therefore, it is reasonable to expect that the hollow-fiber membrane structure prepared with various air-gap distances would be different. The SEM micrographs are shown in Figure 2. It

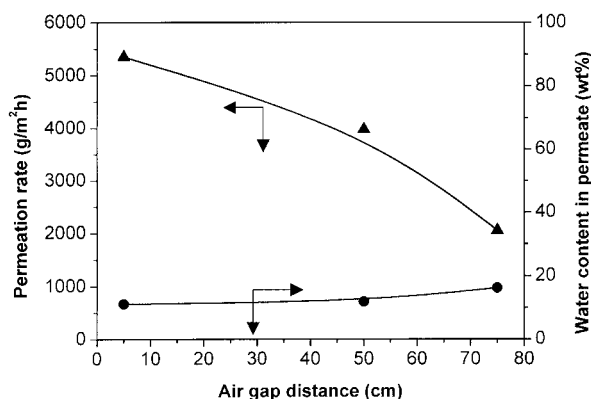


Figure 1 Effect of air-gap distance on the pervaporation performances of CA hollow-fiber membranes. Feed solution: 90 wt % aqueous ethanol solution at 25°C.

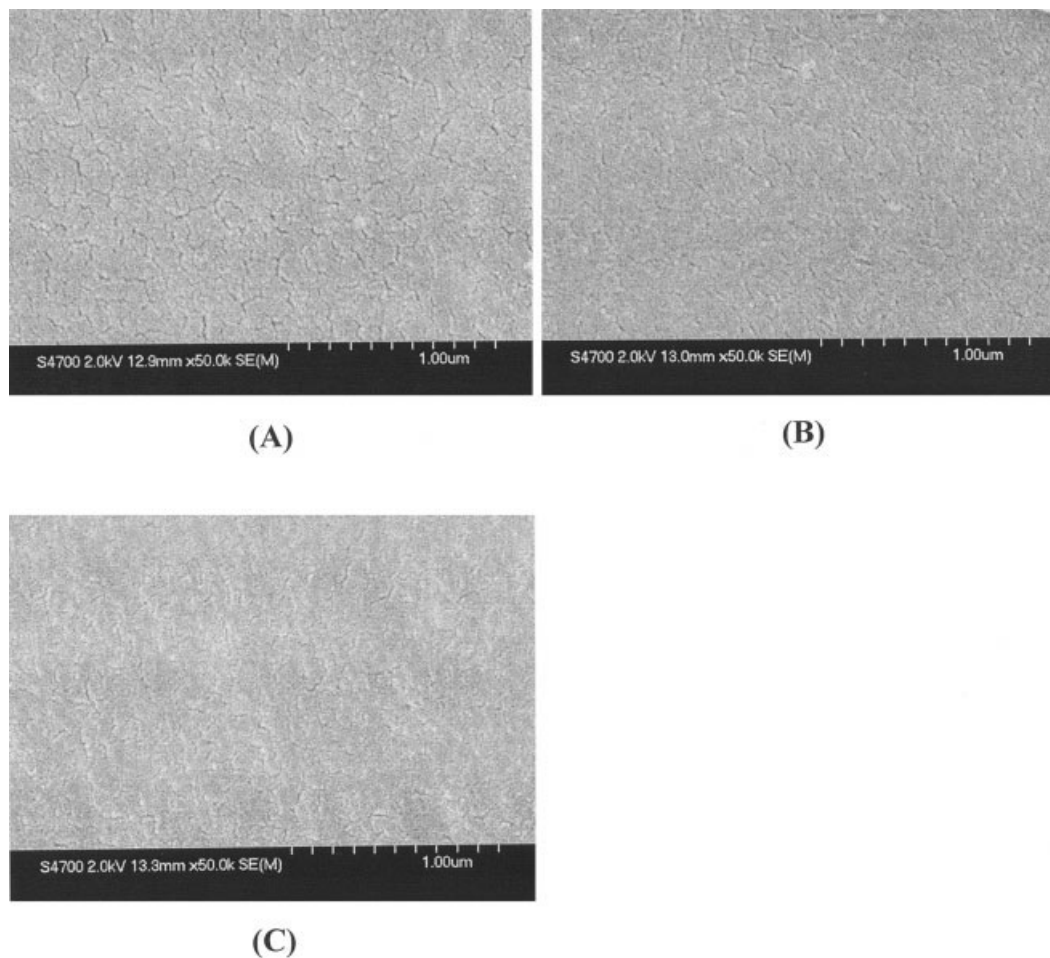


Figure 2 The outer surface SEM image of CA hollow-fiber membranes spun with various air-gap distances. Air-gap distance: (A) 5 cm, (B) 50 cm, and (C) 75 cm.

shows that the outer surface defects of CA hollow-fiber membrane decreases with the air-gap distance increases. This observation agrees well with the results shown in Figure 1. Chung and Hu³² revealed that dry-jet wet-spinning process resulted in external fiber skins with a compact and slightly oriented or stretched structure. Clearly, the orientation of polymer chain is due to the fact that air gap introduces an elongation stress on fiber because of gravity. Because the outer surface of CA hollow-fiber membranes were more compact and oriented as the air-gap distance increases, the result is in the diffusion resistance of the ethanol molecular increases. Thus, the permeation rate decreases as the air-gap distance increases. In addition, even though there is a 75-cm air-gap distance [Fig. 2(C)], there are still some defects on the outer surface of CA hollow-fiber membrane, resulting in the low water content in the permeate. Consequently, optimum pervaporation results were obtained by a CA hollow-fiber membrane spun with a 5-cm air gap. Thus, we use these hollow-fiber membranes to fabricate the CT-*d*-CA composite hollow-fiber membranes.

Effect of chitosan concentration on the pervaporation performances of CT-*d*-CA composite hollow-fiber membranes

To further increase the water selectivity, a hydrophilic polymer CT was introduced to this study. The effect of coating solution concentration on the pervaporation performance of 90 wt % aqueous isopropanol solution through the CT-*d*-CA composite hollow-fiber membrane is shown in Figure 3. The concentration of water in the permeate increases and the permeation rate decreases as the coating solution concentration increases. These results might be due to the fact that an increase in the coating solution concentration leads to a much higher polymer concentration at the surface, resulting in an increase in the coating layer thickness of the composite membrane. This implies that the volume fraction of polymer increases and, consequently, a lower porosity is obtained. Thus, the increase of the water concentration in the permeate results from the increase of the coating layer thickness. Figure 4 reveals the outer layer SEM image of CT-

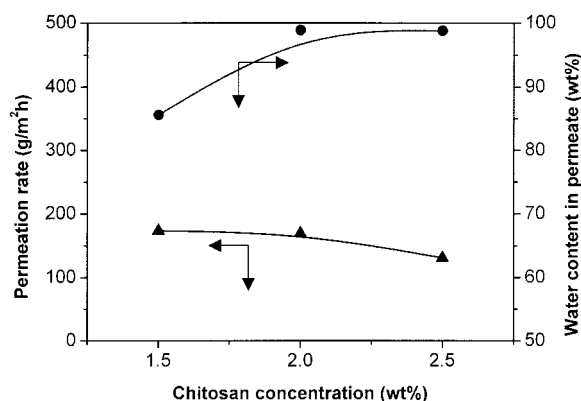


Figure 3 Effect of chitosan concentration on the pervaporation performances of CT-*d*-CA composite hollow-fiber membrane. Feed solution: 90 wt % aqueous ethanol solution at 25°C.

d-CA composite hollow-fiber membranes that were dip-coated by using various concentrations of chitosan. It shows that the thickness of coating layer

increases with an increase in the chitosan concentration. The outer surface defects of CA hollow-fiber membrane can be avoided as increasing the thickness of coating layer. Thus, the permeation rate decreases as the coating solution concentration increases. These observations correspond very well with the results indicated in Figure 3. Furthermore, compared with the uncoated CA hollow-fiber membrane (Fig. 1), the CT-*d*-CA composite hollow-fiber membrane effectively improved the water selectivity.

Pervaporation performances of various aqueous alcohol solutions

The performances of 90 wt % aqueous alcohol mixtures through the CT-*d*-CA composite hollow-fiber membrane by pervaporation are shown in Table II. It can be seen from Table II that the permeation rate of aqueous ethanol solution is higher than that of the aqueous isopropanol solution. Additionally, the water content in permeate of the former is lower than that of the latter. These phenomena might be due to the fact

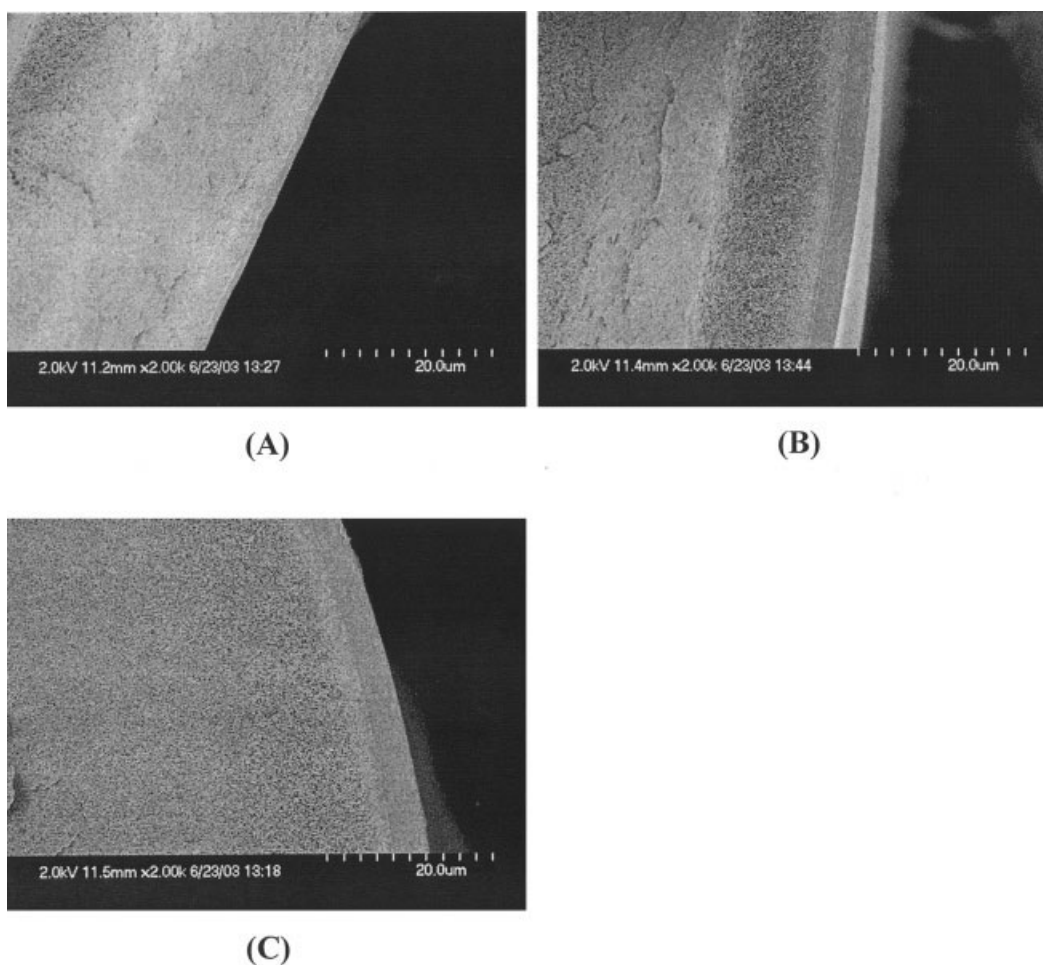


Figure 4 Effect of chitosan concentration on the morphologies of CT-*d*-CA composite hollow-fiber membranes. Chitosan concentration: (A) 1.5 wt %, (B) 2 wt %, and (C) 2.5 wt %.

TABLE II
The Comparison of Feed Solution on the Pervaporation Performances Through CT-*d*-CA Composite Hollow Fiber Membranes

Feed solution	90 wt % Ethanol	90 wt % Isopropanol
Separation performances		
Permeation rate (g/m ² h)	234.0	169.5
Water content in permeate (wt%)	80.1	98.9

that molar volume of ethanol is smaller than molar volume of isopropanol. Furthermore, the interaction between the water molecules and the CT-*d*-CA composite hollow fiber membranes is higher than that of the alcohol, resulting from the higher hydrophilicity of CA.³³ Consequently, the solubility of alcohols for the CT-*d*-CA composite hollow-fiber membrane is lower than that of the water. Meanwhile, the diffusivity of water across the membrane is much higher than the diffusivity of the alcohols.

Effect of feed composition on pervaporation performances

The effect of feed aqueous isopropanol solution composition on the pervaporation performances of the CT-*d*-CA composite hollow-fiber membranes is shown in Figure 5. It shows that the permeation rate increases and the water content in permeate decreases with a decrease in the feed isopropanol concentration. These phenomena might be due to the plasticizing effect of water on the hydrophilic CT-*d*-CA composite hollow-fiber membranes. Generally, hydrophilic membranes have more polar groups and a strong interaction with water through hydrogen bonding or ion-dipoles and

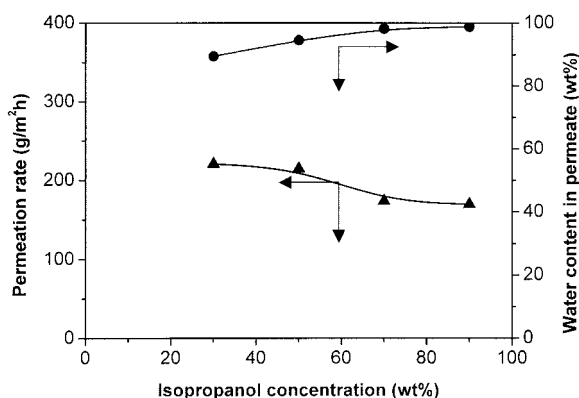


Figure 5 Effect of feed composition on the pervaporation performances of CT-*d*-CA composite hollow-fiber membranes at 25°C. Air-gap distance: 5 cm; Chitosan concentration: 2 wt %.

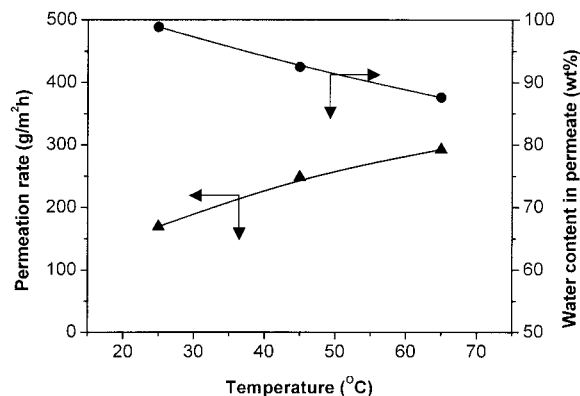


Figure 6 Effect of feed solution temperature on the pervaporation performances of CT-*d*-CA composite hollow-fiber membranes. Air-gap distance: 5 cm; chitosan concentration: 2 wt %.

thereby the selectivity of the membrane to water can be enhanced. When the water concentration in the feed solution is higher, the amorphous regions of the CT-*d*-CA composite hollow-fiber membranes are more swollen. Hence, the polymer chain becomes more flexible and decreases the energy required for diffusive transport through the CT-*d*-CA composite hollow-fiber membranes, resulting in a permeation rate increase, whereas water content in permeate decreased.

Effect of feed solution temperature on pervaporation performance

The effect of feed solution temperature on the pervaporation performance of 90 wt % aqueous isopropanol solution through the CT-*d*-CA composite hollow-fiber membrane is shown in Figure 6. It shows that the permeation rate increases and the water content in permeate decreases as the feed solution temperature increases. These phenomena might be due to the fact that an increase in the swelling of the CT-*d*-CA composite hollow-fiber membrane matrix at higher temperature results in an increase in the free volume, frequency, and amplitude of the polymer chain motions. Thus, the permeation of the permeating molecules through the CT-*d*-CA composite hollow-fiber membrane becomes easier, resulting in an increase in the total permeation rate. This facilitates the transport of isopropanol molecules along with water, thereby reducing the water content in permeate.

CONCLUSION

Pervaporation of alcohol–water mixtures through CT-*d*-CA composite hollow-fiber membranes were investigated in this article. Compared with unmodified CA hollow-fiber membrane, the CT-*d*-CA composite hollow-fiber membrane effectively increases the perm-

selectivity of water. The optimum results for permeation rate and water content in permeate for a 90 wt % aqueous isopropanol solution are 169.5 g/m² h and 98.9 wt %, respectively. The thickness of coating layer increases with increasing chitosan concentration, resulting in the permeation rate decreasing and the water content in permeate increasing.

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